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(54) TWO-PIECE SOLID GOLF BALL

(71) We, UNIROYAL, INC., a corporation organized under the laws of the State of New Jersey, United States of America, of 1230 Avenue of the Americas, New York, New York 10020, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a two-piece solid moulded golf ball.

The invention will be described with reference to the accompanying drawing, wherein:

Figure 1 is a top plan view of a golf ball constructed in accordance with the invention; and

Figure 2 is a cross-sectional view of the internal structure of the ball of Figure 1.

In accordance with the invention a two-piece solid moulded golf ball having remarkably improved flight characteristics compared to prior art two-piece solid moulded golf balls is provided, having a cover comprising ionomer resin composition dimpled on the surface in a particular manner, and a core comprising a mixture of polybutadiene elastomer and a preformed zinc oxide-methacrylic acid reaction product having the constituents combined in the proportions required by basic zinc methacrylate as herein defined.

Ionomer resin compositions suitable for forming the cover of the ball are known. The ionomer resin may be described as an ionic copolymer of an olefin having from 2 to 8 carbon atoms and a metal salt of an unsaturated monocarboxylic acid containing from 2 to 8 carbon atoms. Mixtures of ionomer resins may be used. Small amounts of other materials such as pigments may be included.

Blends of polybutadiene and basic zinc methacrylate type additive suitable for use as the core of the ball are known. The polybutadiene elastomer employed has a cis-1,4-polybutadiene content of 50% or more by weight, perferably at least 80%, and more preferably at least 95%. The basic zinc methacrylate type additive may be described as a preformed reaction product of zinc oxide and methacrylic acid in at least approximately equimolar proportions of zinc oxide to methacrylic acid. Usually the zinc oxide to methacrylic acid molar ratio is from approximately 1:1 to 1.5:1.

The preferred basic zinc methacrylate type additive is preformed by slurrying zinc oxide in a volatile liquid medium (water or an alkanol, e.g., methanol, ethanol), the concentration of zinc oxide in the slurry being from 30 to 65% by weight. While agitating the slurry, the methacrylic acid is added rapidly. The liquid medium serves to dissipate the heat liberated by the exothermic reaction. The liquid medium is removed and the product is dried, usually to a volatile content of 2% or less. The product is finely ground, to a fineness such that at least about 99% passes a 325 mesh (U.S. series) or finer sieve. The product is white in color and usually has a pH of 6.0 to 6.3 in water. The assay of material having zinc oxide and methacrylic acid combined in the ratio required by basic zinc methacrylate is from about 85% to 100%. In thermogravimetric analysis the product usually shows about 3% weight loss at 120°-140°C., an additional 7-13% loss at 180°-240°C., and an additional 30-36% loss at 320°-430°C. In differential thermal analysis there is usually an endothermic peaking in the neighborhood of about 180°C., and a smaller endothermic peak in the neighborhood of about 235°C. Although the product is referred to as "basic zinc methacrylate", this is to imply only that the product contains the zinc and the methacrylic acid mainly in a one-to-one molar ratio. In contrast to this product, the normal salt (zinc dimethycrylate; zinc and methacrylic acid in one-to-two molar ratio) is unsuitable for use in the invention and gives poor results. For purposes of the invention, the basic zinc

methacrylate must be preformed as described, as opposed to formation "in situ" by adding zinc oxide and methacrylic acid to the polybutadiene. Such in situ preparation gives unsatisfactory results.

To make the core composition, the described preformed basic zinc methacrylate type product is blended with the polybutadiene elastomer in conventional rubber mixing equipment, such as a batch internal mixer, an extruder mixer, or an open roll mill, along with any other suitable desired modifying ingredients (e.g., fillers to adjust the specific gravity). From 10 to 60 parts preferably from 25 to 45 parts, of preformed zinc oxide-methacrylic acid reaction product are employed per 100 parts by weight of elastomer.

The core composition further contains, as a cross-linking or curing agent, a source of free radicals such as a peroxide, hydroperoxide, azo compound, or the like. There may be mentioned as suitable for this purpose such free radical curatives as dicymyl peroxide, lauroyl, peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, 2,5-dimethyl-2,4-di(t.butylperoxy) hexane, n-butyl-4,4-bis(t-butylperoxy) valerate, t-butylhydroperoxide, azobisisobutyronitrile, etc. The core composition is shaped into the form of a golf ball core, for example by compression or injection moulding in a golf ball core mould, and the shaped composition is heated at a temperature sufficient to decompose the free-radical generating agent, for a time sufficient to bring about cure. When using n-butyl-4,4-bis(t-butylperoxy) valerate at the peroxide curative, a curing temperature of about 300° to 330°F. is the most desirable. Over-curing is undesirable and under-cure does not produce a good cure. Those skilled in the art of free radical curing agents for polymers know how to adjust the cure time and temperature to obtain optimum results from any specific free radical agent. The elastomer becomes cross-linked during the cure and the methacrylate radical appears to enter into the reaction in some way so as to give enhanced hardness, possibly by bonding the zinc to the polymer.

Other ingredients may be present in the core composition. Thus, an ionomer may be admixed with the core composition, for example in amount of 1 to 30 parts per 100 parts by weight of the elastomer, especially as an aid to better processing, including smoother extrusion and better moulding of the golf ball core. Such ionomer may be described as an ionic copolymer of at least 50 mole percent of one or more alpha-olefins together with a lesser amount of alpha beta ethylenically unsaturated monocarboxylic acid or dicarboxylic acid, the acid monomer content of said copolymer being from 0.2 to 25 mole percent, said copolymer containing uniformly distributed throughout the copolymer a metal ion having an ionized valence of 1 to 3 inclusive in monocarboxylic acid-containing ionomers and a valence of 1 in dicarboxylic acid-containing ionomers. At least 10% (preferably at least about 30%) of the carboxylic acid groups of the copolymer are neutralized by the metal ions and exist in the ionic state. Ionomers based on copolymers of ethylene and acrylic or methacrylic acid are most common. The metal ions are commonly ions of Groups I, II, III, IV-A and VIII of the periodic table, the more common ones being ions of the alkali metals such as sodium and potassium, and the alkaline earth metals such as calcium, strontium, barium and such commonly available metals as zinc and aluminum. The ionomers are hard, transparent, resinous thermoplastic materials.

Other materials such as fillers may also be added to the core compositions, for example litharge or zinc oxide in amount of for example 2 to 20 parts per 100 parts of elastomer, particularly for the purpose of increasing the specific gravity. Other compounding variations may be employed. For example, impact modifiers such as high molecular weight polyethylene may be added.

The thus-moulded unitary core is a sphere having a diameter in excess of approximately 1.515 inches, which is subsequently ground (suitably with the use of a conventional centerless grinder, for example of the Glebar [trademark] type). to a diameter of approximately 1.505 inches. The core has a PGA hardness of approximately 65, measured on a conventional golf ball PGA hardness testing machine fitted with a 0.180 inch thickness skin to compensate for the smaller diameter of the core compared with a 1.680 inch diameter golf ball. The core has a rebound of at least 75% and a specific gravity of approximately 1.20.

The cover composition for the present golf ball is, as indicated above, an ionomer resin, or a blend of ionomer resins (e.g. sodium copolymer "Surlyn [trademark] 1555" plus zinc copolymer "Surlyn 1557") of the kind described. A small amount of pigment (e.g., titanium dioxide) is added to make the cover compound opaque.

To form the dimpled cover of the unitary moulded ball of the invention, the cover composition is applied by injection moulding directly onto the previously described core suspended by pins within a mould cavity. For this purpose a conventional retractable-pin mould, commercially available from Osley and Whitney Co., may be used. The cover is of sufficient thickness to produce a golf ball of approximately 1.680 inches minimum diameter. The injection moulding sprue is removed from the ball and the ball is then centerless

ground to remove gates and flash. The grinding or deflashing operation improves the flight characteristics of the ball. However, excessive grinding can unduly alter the width and depth of the dimples and impair the flight characteristics. The amount of grinding that would normally be just sufficient to remove the flash is ordinarily also sufficient to provide optimum flight characteristics.

As indicated above, an important feature of the golf ball of the invention resides in the dimpled surface pattern on the cover, imparted during the moulding of the cover. Referring to the drawing, the outer surface 10 of the golf ball cover 11 injection moulded over the core 12 has a dimple pattern consisting of 252 dimples 13 which are circular in cross section. The mould dimensions for the dimples are 0.160 inch in diameter by 0.0145 inch deep, the dimples being arranged in an icosahedral array. The dimples or bowl shaped depressions are uniformly distributed about the surface of the core, and generate an icosahedral lattice of equilateral spherical triangles each containing an equal number of depressions. All circumferential pathways of substantial width (0.005 inch or greater) that may be circumscribed about the ball (except that at the flash line [parting line], which is the equator of the ball) will intersect several of the depressions. The air stream rushing over the surface of the ball in flight contacts the dimples, causing the ball to exhibit improved aerodynamic characteristics. The dimples occupy approximately fifty percent of the area of the ball surface. Such a surface pattern is known.

In specifying the surface desired in a ball, it is accepted practice in the art to specify mould dimensions rather than ball dimensions bcause of the variability inherent in the product of molds and balls. A certain amount of shrinkage occurs, and the grinding operation to which the ball is subjected further alters the dimensions of the moulded ball somewhat. Furthermore, the coating of paint applied to the ball slightly alters the surface. However, any discrepancies which may occur in the ultimate surface of the ball from that provided on the mould are small, and the exigencies of ball production make it acceptable and desirable to specify the ball surface in terms of the mould dimensions, with the understanding that in the final ball the dimensions are slightly different. Accordingly, it will be understood that throughout this specification and claims the ball surface is to be achieved by providing a mould having the stated dimensions, and that a ball produced in the described manner using such a mould will have substantially the optimum desirable dimensions after deflashing and painting.

The ball has superior flight performance (greater flight carry) to comparable previous two-piece golf balls. The golf ball of the invention is remarkable for its advantageous feel off the club, and the ball has the other properties highly desired in a golf ball including initial velocity, click, durability, rebound, compression, etc.

The following example will serve to illustrate the invention in more detail.

The following master batch for the golf ball core stock is prepared in a Banbury [trademark] mixer (all quantities shown herein being expressed in parts by weight):

Core Stock Masterbatch

Polybutadiene elastomer	80
Ionomer resin	20
Ground Calcium carbonate	3.94
Titanium dioxide (Rutile)	1.60
"Basic zinc methacrylate"	31.07
Trimethyl propane trimethacrylate	5.11
Litharge	8.90
White lead No. 202	5.93
	156.55

The polybutadiene elastomer is Mitsui BROI [trademark] rubber, 97% cis content. The ionomer resin is Surlyn [trademark] 1555, an ionic copolymer of approximately 96.5 mole-percent of ethylene and 3.5 mole-percent of methacrylic acid, with sodium ions uniformly distributed throughout the copolymer to an extent representing about 50% neutralization of the methacrylic acid, ASTM melt index of 10. The ground calcium carbonate is the commercial material Camel White [trademark]. The titanium dioxide is the commercial material Titanium Ranc [trademark]. The "basic zinc methacrylate" is the preformed reaction product of zinc oxide and methacrylic acid in substantially equimolar quantities, as described above.

The final core compound is made by mixing the above core stock masterbatch with curative on a mill as follows:

Final Core Stock

Core stock masterbatch (as above)	156.65
Peroxide curative	7.20
Blue color	0.058

The peroxide curative is Percadox [trademark] 17/40, which is 40% active n-butyl 4,4-bis (t-butylperoxy) valerate on calcium carbonate. The blue color serves as an indicator of completeness of mixing.

A slug of the core stock is moulded into spherical shape by compression moulding and curing for 18-20 minutes at about 320°F. The moulded sphere is approximately 1.64 inches in diameter; it is ground in the centerless grinder to a diameter of approximately 1.505 inches.

The cover composition is prepared by mixing the following ingredients:

Cover Composition

Surlyn 1555	50
Surlyn 1557	50
Titanium dioxide	1

The Surlyn 1555 is as described previously; Surlyn 1557 is similar but contains zinc as the metal in place of sodium. The cover is injection moulded directly onto the core while the core is suspended in the center of a spherical mould cavity larger than the core, the core being suspended concentrically of the mould cavity by five retractable pins in each half of the two-part mould. The cover stock is injection moulded at a moulding machine temperature of 475°F into the mould which is cooled to a temperature of 40-60°F. There are eight points of injection spaced around the equatorial parting line of the mould. As the space defined between the inner surface of the mould and the outer surface of the core becomes filled with cover stock, the pins are withdrawn. It will be understood that the surface of the mould cavity is provided with convex protrusions of the dimensions indicated above for forming the dimple pattern in the outer surface of the cover. The inner end of each retractable pin is rounded so that when it is withdrawn to the plane of the mould surface it serves to form a dimple on the surface of the cover in the conventional way. The dwell time in the mould is thirty seconds. The ball is removed from the mould and degated, and centerless ground to remove flash. As indicated previously this deflashing operation also improves the flight characteristics of the ball. After wet blasting with 220-400 grit Carborundum [trademark] and scrubbing, the ball is primed, painted and decorated in the usual manner.

The final average diameter of the ball is approximately 1.680 inches (as compared to approximately 1.682 inches before grinding). The PGA hardness is 88, the weight is 1.612 ounces. Rebound is 75%.

The flight characteristics of the ball may be determined with the aid of a hitting machine. In such a test with the machine adjusted to simulate professional conditions, balls of the invention showed a carry of 203.4 yards, and a total distance (carry plus roll) of 265.2 yards. This compares to a carry of 198.8 yards and a total distance of 261.5 yards for comparable conventional two-piece solid balls with 336 dimples on the surface. With the hitting machine adjusted to less severe average player conditions the balls of the invention had a carry of 185.0 yards and a total distance of 255.2 yards, as compared to a carry of 181.3 yards and a total distance of 252 yards for the conventional balls under the same conditions.

WHAT WE CLAIM IS:

1. A solid two-piece moulded golf ball comprising a spherical core having a diameter of approximately 1.505 inches, a PGA hardness of approximately 65, a rebound of at least 75% and a specific gravity of approximately 1.20. the said core comprising a cross-linked composition containing 100 parts by weight of polybutadiene elastomer having a cis-1,4-polybutadiene content of at least 50% by weight and from 10 to 60 parts by weight of preformed zinc oxide-methacrylic acid reaction product in which the zinc oxide and methacrylic acid are combined in the proportions required by basic zinc methacrylate as hereinbefore defined, said core composition containing a free radical generating curing agent in amount sufficient to cure the composition, the said core being surrounded by a cover composition of sufficient thickness to provide a ball diameter of approximately 1.680 inches, said cover composition comprising a thermoplastic resinous ionic copolymer of an

olefin having from 2 to 8 carbon atoms and a metal salt of an unsaturated monocarboxylic acid containing from 2 to 8 carbon atoms, the outer surface of the said cover having a dimple pattern consisting of 252 dimples circular in cross-section, the dimensions of the dimples expressed as mould dimensions being 0.160 inch in diameter by 0.0145 inch deep, said dimples being arranged in an icosahedral array uniformly distributed on the surface of the ball and covering approximately fifty per cent of the area of the ball surface, the moulded ball having been deflashed by centerless grinding.

2. A solid two-piece moulded golf ball substantially as herein described with reference to the accompanying drawings.

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1595477 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

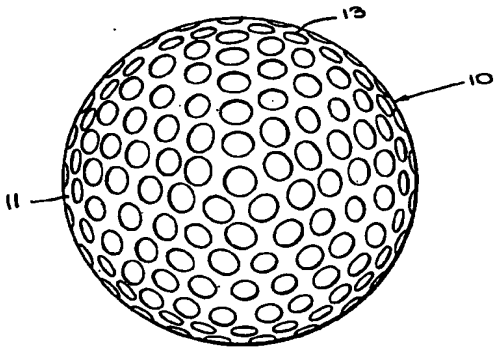

Fig.1.

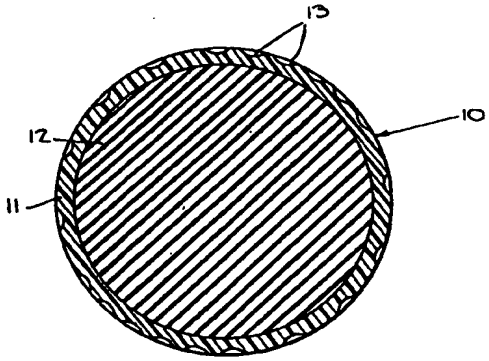

Fig.2.